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UNDERGLAZE ENGOBE FOR CERAMIC FACING TILES

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A formula for white underglaze engobe is developed based on porcelain-faience waste (after the first firing) to be used on facing tiles with a dark-colored ceramic base. Applying this engobe to a dried tile ensures good sinterability of the engobe to the tile at higher temperatures of the first firing. This makes it possible to simplify the engobe composition and to improve the quality parameters of the tile itself and of the glaze coating.

When ceramic tiles for interior wall decoration are produced from local red-burning clays and industrial waste, the base of the ceramic tile, as a rule, has a dark color which requires an elevated consumption of expensive glaze and opacifier. A solution for this problem can be found in applying a white underglaze layer (engobe) whose composition is based on inexpensive materials and developing a technology for its deposition on tiles.

The existing compositions and technology for depositing engobe on fired tiles before glazing have several disadvantages related to the multicomponent compositions using easily sintering materials (as a rule, frits) [1]. This is caused by the requirement to match the engobe sintering temperature and the glaze spreading temperature, as well as more stringent requirements on the flow properties of the engobe slip, such as good fluidity combined with sufficiently high density.

To produce low-shrinkage and stronger tiles with the anorthite structure, the current practice calls for adding calcium carbonate into the mixtures, which increases the water absorption of ceramics [2, 3]. This change in the structure impairs the quality of the glaze coating.

We have developed engobe formulas and a technology for their deposition of predried tiles and their subsequent sintering to the tile surface at the higher temperatures $(1050-1150^{\circ}\text{C})$ of the first firing. In this case a surface layer with preset water absorption and increased whiteness is formed.

The main component for developing engobe compositions with increased whiteness was the waste (after the first firing) generated by the porcelain and faience industry. To bond the engobe layer to the tile surface and to make the engobe slip steadier, white-burning clay and carboxymethyl cellulose (CMC) were introduced into the mixture. The sintering of engobe with the tile surface depends on the first

firing temperature and is controlled by adding clear glass cullet or a boron-bearing component into the engobe composition. The engobe contains (wt.%): 70-80 porcelain-faience production waste; 10-20 white-burning clays, up to 0.2 CMC, and 20-30 cullet. The chemical composition of the initial components is listed in Table 1.

An engobe slip of moisture 55-57%, density 1.34-1.38 g/cm³, and time of efflux from a viscosimeter (hole diameter 4 mm) equal to 11-12 sec was prepared by moist milling in a ball mill to a residue of 1.5-2.0% on a sieve No. 0063.

Engobe was deposited on a dry tile surface by spraying. In this case the sprayer should finely disperse the engobe, producing a smooth engobe layer.

In industrial conditions engobe was deposited on tiles by the spraying method in the break between the sectors of a one-row roller drier. The tile temperature was $80-90^{\circ}\text{C}$, the residual moisture 2-3%, and the engobe consumption 0.02-0.04 g/cm² for an engobe layer thickness of 250-300 µm.

After the final drying in the last sector of the drier at a temperature of $200-250^{\circ}\text{C}$ the tiles arrived at the roller kiln for the first firing. The firing duration is 20-40 min at the maximum temperature of $1030-1150^{\circ}\text{C}$ and depends on the furnace length and the material of the roller conveyor.

In developing the engobe composition we investigated the physicomechanical properties of fired engobe mixtures and of coated tiles. For this purpose a plastic mixture was obtained from the engobe slip by partial dehydration and was used to mold samples of sizes $3 \times 20 \times 60$ mm, which after drying were subjected to fast firing in the kiln.

The initial composition contained 100% faience scrap after the first firing and a CMC solution as the binding component. Firing within a temperature range of $1000-1150^{\circ}\text{C}$ produced a material with water absorption of 18.7-25.3% and bending strength of 1.2-11.5 MPa. Using glass cullet as

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414 A. I. Nestertsov

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Material	Weight content, %							
	SiO ₂	Al_2O_3	Fe_2O_3	CaO	MgO	K ₂ O	Na ₂ O	calcination loss
Veselovskoe clay*	56.60	29.80	0.80	0.49	0.71	1.55	0.50	8.85
Broken porcelain and faience	75.12	23.18	0.61	0.49	0.45	_	_	_
Glass cullet	66.51	5.19	2.02	8.23	2.27	7.07	8.00	_
Datolite concentrate**	32.30	1.20	3.01	35.60	0.24	1.75	_	7.10

^{*} Veselovskoe clay also contains 0.70% TiO₂.

a sintering additive yields samples with water absorption of 12.6-16.7%, bending strength of 26.0-30.3 MPa, and whiteness of 80-82% compared to a reference standard plate made of chemically pure barium sulfate. The degree of whiteness of coatings was determined on a photometric device. i.e., a FB-2 luster meter.

The introduction of a boron-bearing component instead of cullet into the mixture decreases water absorption to 6.0-7.2% and increases bending strength to 32.0-37.2 MPa. The whiteness is equal to 78-80%.

To determine the degree of coordination between engobe mixtures and the ceramic tile substrate, TCLE values were determined and found to be equal to $(5.50-5.59) \times 10^{-6} \, \mathrm{K^{-1}}$ for engobe and $6.1 \times 10^{-6} \, \mathrm{K^{-1}}$ for the tile. The discrepancy is 8.3-9.3%, which is within admissible limits.

The x-ray structural analysis demonstrated the identity of the phase compositions of the engobe and the tiles, with the engobe having a lower content of quartz and cristobalite. Such phase composition improves the physicomechanical properties of the engobe coating. The quality of the sintering of the engobe coating with the ceramic base of the tile was estimated based its resistance to frost, thermal resistance, and the rate of water absorption by the tile surface. After 100 cycles of alternate freezing and heating, no flaking or spalling of engobe was observed, and after 25 cycles of standard cy-

cling no microcracks appeared on the surface. The rate of absorption of a drop of water by the engobe-coated tile surface is lower than that of an uncoated tile and is controlled by the engobe composition and the sintering degree.

After the first firing the engobed tile was glazed by casting, with different amounts of glaze consumption. The decrease in the glaze consumption by 30% compared to the tile without the engobe coating yields a glaze coating whose aesthetic and qualitative parameters are not inferior to those of the reference standard tile. The glaze has good luster, spreading, and meet the requirements of GOST 6141–91.

The developed engobe compositions and the deposition technology have been tested under industrial conditions at the Stary Oskol, Kharkov, and Kiev ceramic works.

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^{**} Datolite concentrate also contains 18.80% B₂O₃.